

# Infrared luminescence in Bi-doped Ge-S and As-Ge-S chalcogenide glasses and fibers

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Experimental and theoretical studies of spectral properties of chalcogenide Ge-S and As-Ge-S glasses and fibers are performed. A broad infrared (IR) luminescence band which covers the 1.2–2.3  $\mu\text{m}$  range with a lifetime about 6  $\mu\text{s}$  is discovered. Similar luminescence is also present in optical fibers drawn from these glasses. Arsenic addition to Ge-S glass significantly enhances both its resistance to crystallization and the intensity of the luminescence. Computer modeling of Bi-related centers shows that interstitial  $\text{Bi}^+$  ions adjacent to negatively charged S vacancies are most likely responsible for the IR luminescence.

## I. INTRODUCTION

During the last decade Bi-doped bulk glasses and optical fibers have attracted a lot of interest due to their characteristic broadband IR luminescence in the 1–1.7  $\mu\text{m}$  range which has a potential for new broadband fiber amplifiers and lasers [1]. Despite a successful demonstration of laser generation and optical gain in the 1.15–1.55  $\mu\text{m}$  range using silica-based optical fibers with different dopants [2], the origin of active Bi-related centers in optical materials is still controversial. IR luminescence from such centers has been observed in different types of glasses and crystals, and the spectral properties of infrared (IR) luminescence have similar features. The available experimental data suggest that Bi luminescent centers have similar origin in different hosts. Besides there are reasons to believe that there are several active centers in the glass sample and the ratio between them depends on the host and on production technology.

Certain properties of chalcogenide glasses [3] make them, on the one hand, promising materials for various optical devices and applications including fiber optics, and on the other, convenient hosts for optical transitions research, in particular for the luminescence studies. These properties include a wide transparency range (from visible to middle-IR) that depends on glass composition, high refractive index, and high nonlinear susceptibility. The important features of these glasses are an ability to be doped with rare-earth elements and promising luminescence characteristics of rare-earth active centers [4–6]. Low phonon energy allows radiative transitions in the middle-IR region (with wavelengths beyond 2  $\mu\text{m}$ ). A significant number of chalcogenide glasses shows good chemical resistance, especially to atmospheric water. It is also possible to obtain glasses with a wide variety of properties depending on their composition.

Chalcogenide glasses allow one to research the origin of Bi-related IR luminescence, previously studied in the fol-

lowing glass systems:  $\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--KBr}$  [7],  $\text{GeS}_2\text{--Ga}_2\text{S}_3$  [8], and  $\text{Ga}_2\text{S}_3\text{--La}_2\text{S}_3\text{--La}_2\text{O}_3$  [9]. In [7, 8] bismuth in low-valence states, such as  $\text{Bi}^+$ , was supposed to be responsible for the IR luminescence. Based on calculation results [10], bismuth dimers were considered in [9] as possible sources of the IR luminescence.

For our research we chose two glass systems: Ge-S and As-Ge-S. The first was used for studying the influence of Ge/S ratio on luminescence intensity. The second system is far more resistant to crystallization, and so it is suitable for fiber drawing. We also compared our experimental results with Ga-Ge-S glass studied earlier.

## II. EXPERIMENT

Metallic Bi doped bulk glass samples (concentrations 0.05, 0.5, 1 at.%), as well as samples without Bi were synthesized from high-purity Ge, Ga, As, S in evacuated quartz ampules with inner diameter 10–12 mm in a rocking muffle furnace at 800–850  $^\circ\text{C}$ . For observation of luminescence dependence on synthesis temperature Ge-S samples were synthesized at 700  $^\circ\text{C}$ . The times of cooling and annealing of Ge-S and As-Ge-S glasses were 2 and 15 hours, respectively [11].

For spectroscopic studies we used 2–3 mm thick optically polished bulk samples and 300  $\mu\text{m}$  fibers drawn by the crucible method. The transmission spectra of bulk samples were measured on a Perkin-Elmer Lambda 900 spectrometer. Semiconductor laser sources with fiber output at 975 nm and 1064 nm wavelengths were used as excitation sources. The output end of the fiber was fixed at a focal point of the lens, and collimated beam was used for luminescence excitation in the bulk samples. A setup consisting of a Hamamatsu P7163 InAs photovoltaic detector, an MDR-2 monochromator, a collimator, and an SR830 Stanford Research lock-in amplifier was used to measure the luminescence spectra. This equipment was

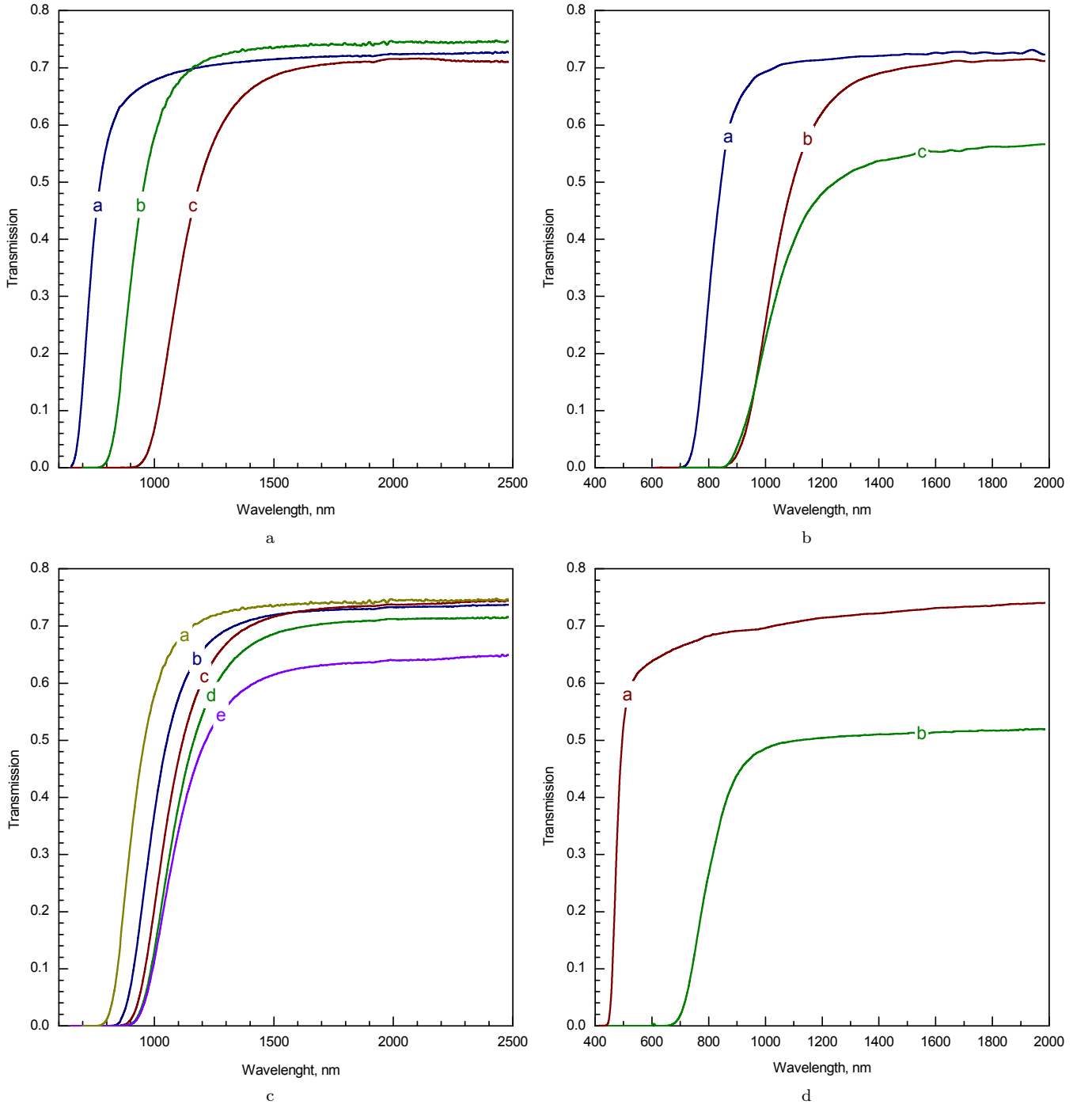


FIG. 1. Transmission spectra. a. As-Ge-S glasses with different Bi concentration: (a)  $\text{As}_{10}\text{Ge}_{36}\text{S}_{54} + 0.05\% \text{ Bi}$ , (b)  $\text{As}_{10}\text{Ge}_{35}\text{S}_{55} + 0.5\% \text{ Bi}$ , (c)  $\text{As}_{10}\text{Ge}_{36}\text{S}_{54} + 1\% \text{ Bi}$ ; b. Ge-S glasses: (a)  $\text{GeS}_{1.35}$ , (b)  $\text{GeS}_{1.35} + 1\% \text{ Bi}$ , (c)  $\text{GeS}_{1.5} + 1\% \text{ Bi}$ ; c. As-Ge-S glasses with different As content: (a)  $\text{As}_{10}\text{Ge}_{35}\text{S}_{55} + 0.5\% \text{ Bi}$ , (b)  $\text{As}_5\text{Ge}_{38}\text{S}_{57} + 0.5\% \text{ Bi}$ , (c)  $\text{As}_2\text{Ge}_{39.2}\text{S}_{58.8} + 0.5\% \text{ Bi}$ , (d)  $\text{AsGe}_{39.6}\text{S}_{59.4} + 0.5\% \text{ Bi}$ , (e)  $\text{As}_{0.5}\text{Ge}_{39.8}\text{S}_{59.7} + 0.5\% \text{ Bi}$ ; d. Ga-Ge-S glasses: (a)  $80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3$ , (b)  $80\text{GeS}_2\text{-}20\text{Ga}_2\text{S}_3 + 1\% \text{ Bi}$ .

able to obtain spectra in the 1–2.4  $\mu\text{m}$  range with a resolution of up to 4 nm. Samples were measured at 293–298 K temperature.

The transmission spectra of glass samples with different composition are shown in Fig. 1. One can see how the

short-wave transmission edge depends on the glass composition and Bi content. Increasing the Bi concentration shifts the short-wave edge to the IR region (Fig. 1(a)). The  $\text{GeS}_{1.5}:\text{Bi}$  sample has a lower transmission than the  $\text{GeS}_{1.35}$  sample without Bi (Fig. 1(b)). This fact may be

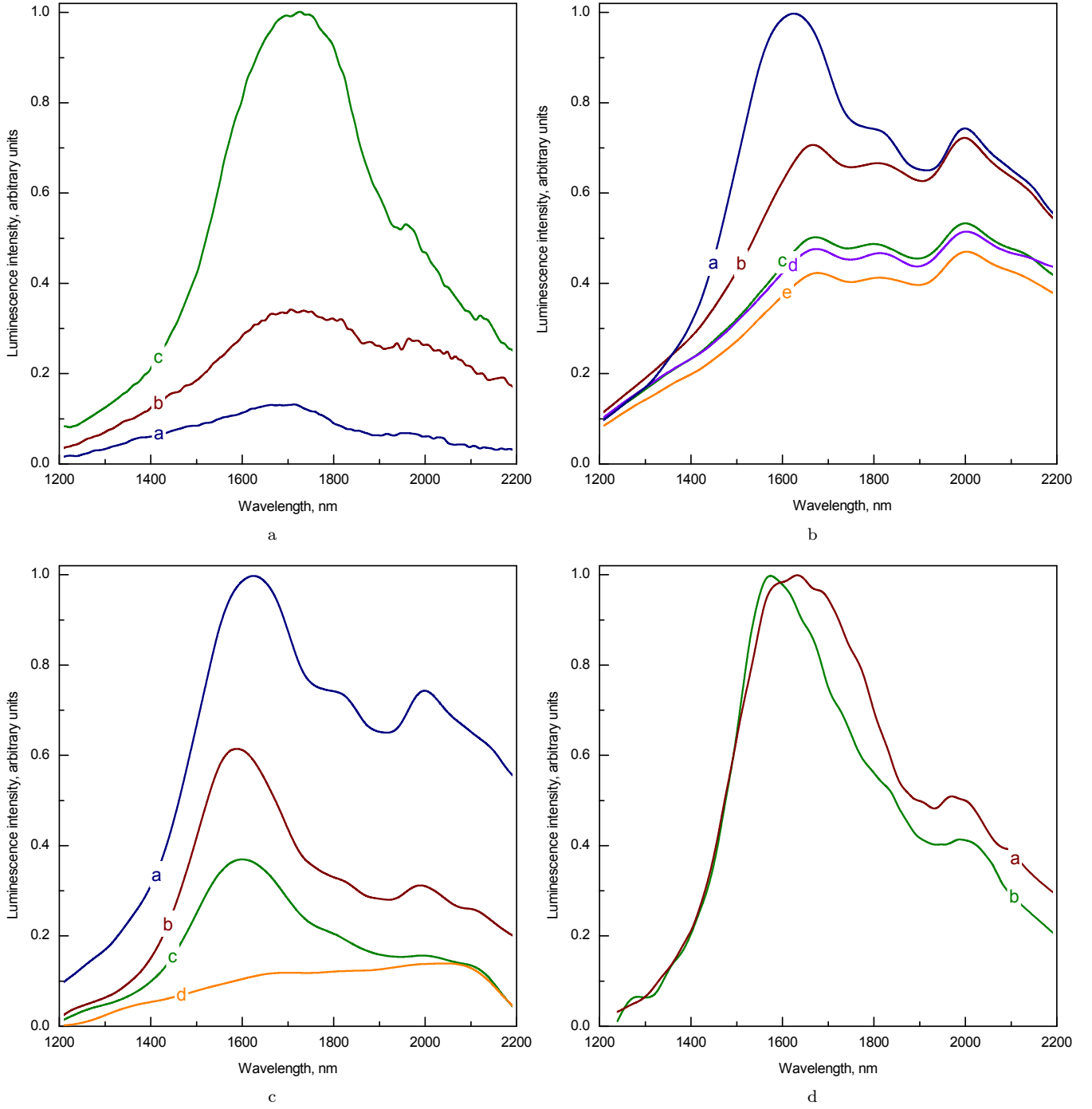


FIG. 2. Luminescence spectra. a. Ge-S glasses (excitation at 1064 nm): (a)  $\text{GeS}_{1.35} + 1\% \text{ Bi}$ , (b)  $\text{GeS}_{1.5} + 1\% \text{ Bi}$ , (c)  $\text{As}_{10}\text{Ge}_{35}\text{S}_{55} + 0.5\% \text{ Bi}$ ; b. As-Ge-S glasses with various As content (excitation at 975 nm): (a)  $\text{As}_{10}\text{Ge}_{35}\text{S}_{55} + 0.5\% \text{ Bi}$ , (b)  $\text{As}_5\text{Ge}_{38}\text{S}_{57} + 0.5\% \text{ Bi}$ , (c)  $\text{As}_2\text{Ge}_{39.2}\text{S}_{58.8} + 0.5\% \text{ Bi}$ , (d)  $\text{AsGe}_{39.6}\text{S}_{59.4} + 0.5\% \text{ Bi}$ , (e)  $\text{As}_{0.5}\text{Ge}_{39.8}\text{S}_{59.7} + 0.5\% \text{ Bi}$ ; c. As-Ge-S glasses (excitation at 975 nm): (a)  $\text{As}_{10}\text{Ge}_{35}\text{S}_{55} + 0.5\% \text{ Bi}$ , (b)  $\text{As}_{20}\text{Ge}_{30}\text{S}_{50} + 0.5\% \text{ Bi}$ , (c)  $\text{As}_{10}\text{Ge}_{36}\text{S}_{54} + 0.05\% \text{ Bi}$ , (d)  $\text{As}_{10}\text{Ge}_{36}\text{S}_{54} + 1\% \text{ Bi}$ ; d. As-Ge-S fiber samples (excitation at 975 nm, the spectra are normalized to 1): (a)  $\text{As}_{10}\text{Ge}_{35}\text{S}_{55} + 0.5\% \text{ Bi}$ , (b)  $\text{As}_{20}\text{Ge}_{30}\text{S}_{50} + 0.5\% \text{ Bi}$ .

due to the refractive index increase and a formation of inhomogeneities due to a partial crystallization. Addition of As expands the transmission range and increases the transmission (Fig. 1(c)), which may be related to an

increase in resistance to crystallization. In the transmission spectra of the samples with Bi there are no distinctly expressed absorption bands.

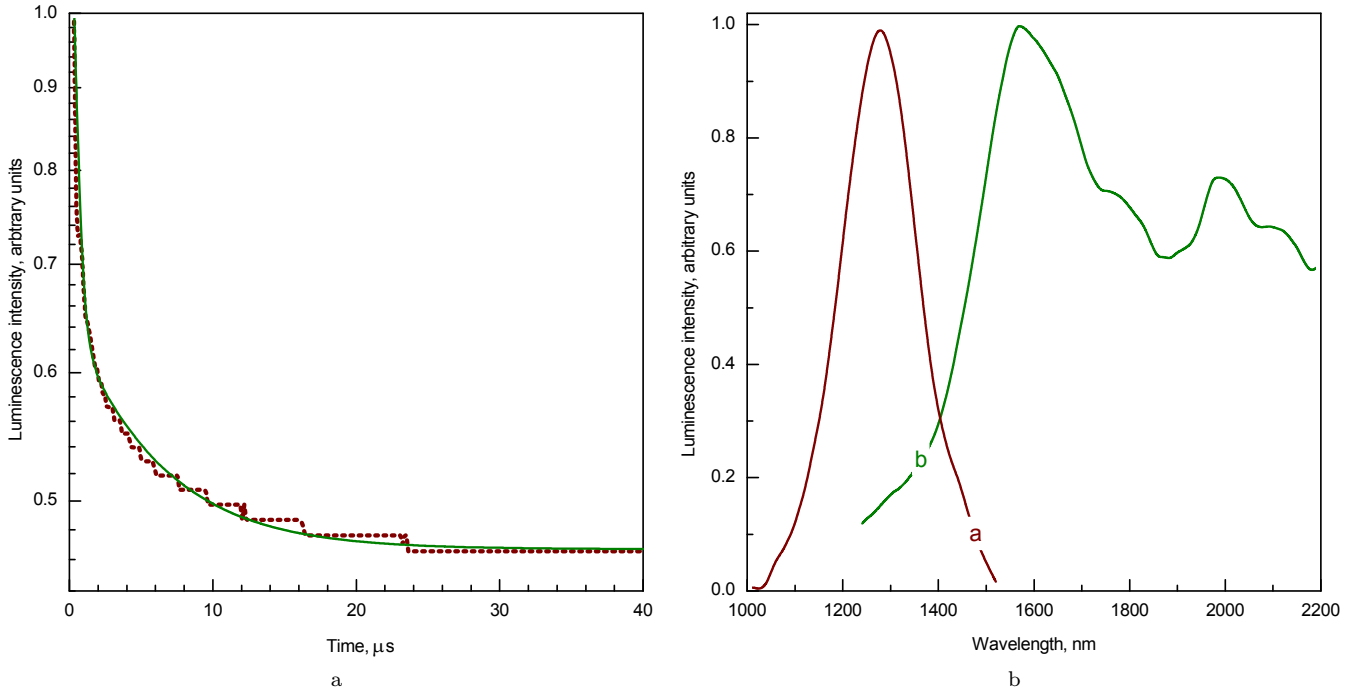


FIG. 3. a. Luminescence decay curve ( $\text{As}_{10}\text{Ge}_{35}\text{S}_{55} + 0.45\% \text{ Bi}$ , excitation at 975 nm):  $\tau_1 \approx 0.3 \mu\text{s}$ ,  $\tau_2 \approx 5.7 \mu\text{s}$ . b. Luminescence spectra of (a)  $80\text{GeS}_2-20\text{Ga}_2\text{S}_3 + 0.5 \text{ at.}\% \text{ Bi}$  glass (excitation at 839 nm); (b)  $\text{As}_{10}\text{Ge}_{35}\text{S}_{55} + 0.5 \text{ at.}\% \text{ Bi}$  glass (excitation at 975 nm, the spectra are normalized to 1).

Ga-Ge-S system glasses doped with Bi were also studied. Bulk samples of such glasses easily crystallize even when they are cooled in cold water. Therefore it is extremely difficult to make optical fibers using this glass composition. Ga-Ge-S system glasses are more transparent in the visible range than As-Ge-S and Ge-S system glasses, but Bi addition makes them far more less transparent. The absorption edge is significantly shifted towards shorter wavelengths in such doped glasses (Fig. 1(d)).

The luminescence spectra of glass samples with different composition are shown in Fig. 2. Ge-S glasses demonstrate a relatively low luminescence band intensity, but its width covers a wide spectral range (Fig. 2(a)).  $\text{GeS}_{1.5}$  glass has a higher luminescence intensity than  $\text{GeS}_{1.35}$ . We couldn't obtain Bi-doped Ge-S glass with higher S content because of too strong a tendency to crystallization. It is known that the well-studied As-S glass system shows no tendency to crystallization, and it was decided to add As into the Ge-S system to increase the glass-forming ability of Ge-S system glasses. The S/Ge ratio was no higher than 2. Also As addition resulted in a significant increase in the luminescence intensity (Figs. 2(a) and 2(b)).

Measurements of the concentration series of samples (Figs. 2(b) and 2(c)) with various proportion of As and Bi have shown that the maximum intensity of the IR luminescence band occurs in the  $\text{As}_{10}\text{Ge}_{35}\text{S}_{55} + 0.5 \text{ at.}\% \text{ Bi}$  glass. Slightly lower intensity is observed in  $\text{As}_{20}\text{Ge}_{30}\text{S}_{50} + 0.5 \text{ at.}\% \text{ Bi}$  glass.

Arsenic presumably affects mainly the resistance to crystallization and the intensity of luminescence, but does not change its spectral structure. Arsenic unlikely leads to the formation of new centers of luminescence absent in Ge-S.

Similar luminescence bands were also detected in optical fibers made of the same glass (Fig. 2(d), to be compared with Fig. 2(c)).

The luminescence lifetime was about  $6 \mu\text{s}$  (Fig. 3(a)).

In Ga-Ge-S glasses the IR luminescence band maximum is located near  $1.28 \mu\text{m}$  (Fig. 3(b)), and the band shape is close to Gaussian with FWHM about 200 nm. Band intensity is comparable to that in As-Ge-S glasses. Disadvantages of these glass systems compared with As-Ge-S glasses consist in much higher tendency to crystallization and a relatively narrow IR luminescence band.

### III. MODELING OF BI-RELATED LUMINESCENCE CENTERS

To understand the origin of Bi-related centers responsible for the IR luminescence observed in  $\text{GeS}_{2-x}$  glasses and based on assumptions on the role of subvalent bismuth states [12], we performed computer simulation of the structure and absorption spectra of several centers most probably formed by Bi atoms in  $\text{GeS}_{2-x}$  glass network. Namely, trivalent ( $\text{Bi}^{3+}$ ) and divalent ( $\text{Bi}^{2+}$ ) substitutional Bi centers, interstitial  $\text{Bi}^+$  ions, interstitial  $\text{Bi}^0$  atoms, and complexes formed by an interstitial Bi

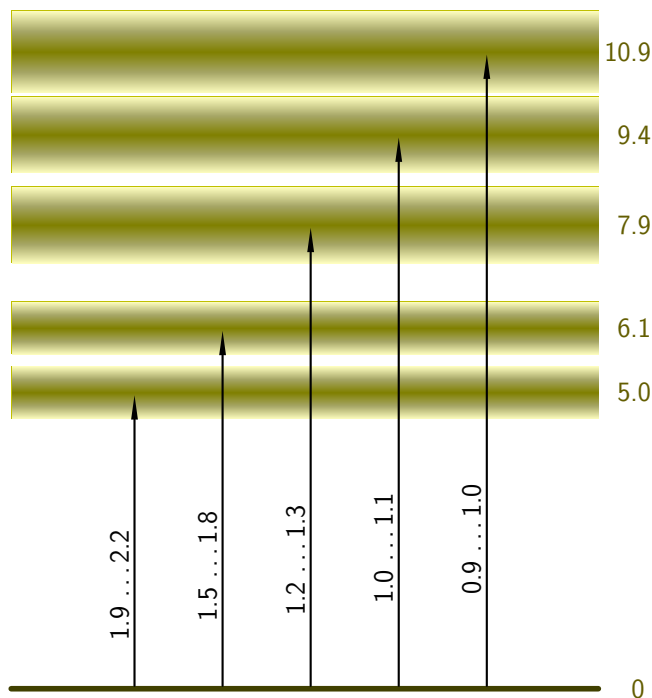


FIG. 4. Calculated levels and transitions in the complex formed by an interstitial Bi atom and an S vacancy (energy in  $10^3 \text{ cm}^{-1}$ , transition wavelengths in  $\mu\text{m}$ ).

atom and an S vacancy were studied. The structure of the centers was calculated using network models with periodic boundary conditions. The unit cell of defect-free  $\text{GeS}_2$  network containing 24  $\text{GeS}_2$  groups was prepared by ab initio (Car-Parrinello) molecular dynamics. To study Bi-related centers, a Bi atom was placed in the central part of the unit cell. S vacancies were formed by removal of one of the S atoms. The charge state of a center was determined by the total unit cell charge. Equilibrium configurations of Bi-related centers were found by a complete geometry optimization with the gradient method in the plane wave basis using the generalized gradient approximation of the density functional theory and pseudopotentials. All the structure-related calculations were performed with the Quantum-Espresso package [13]. The configurations of Bi-related centers were used further to calculate the absorption spectra of the centers using the Bethe-Salpeter equation method based on the all-electron full-potential linearized augmented plane wave approach taking into account the spin-orbit interaction essential for Bi-containing systems. The Elk code [14] was used in spectra calculations. To estimate the luminescence Stokes shift, the configurational coordinate diagrams of Bi-related centers were studied in the frame of a simple model. The modeling is described in detail in Refs. [15, 16].

The modeling shows that threefold and twofold coordinated Bi atoms bonded with Ge atoms by three or two bridging S atoms, respectively ( $\text{Bi}^{3+}$  or  $\text{Bi}^{2+}$  centers),

are very likely to occur in  $\text{GeS}_2$  network. In such centers bismuth is in three- and divalent state, respectively. Formation energy estimations based on the calculated total energies of corresponding unit cells show that  $\text{Bi}^{3+}$  centers are favorable. Calculated wavelengths of the absorption bands of such  $\text{Bi}^{3+}$  and  $\text{Bi}^{2+}$  centers in  $\text{GeS}_2$  network agree well with the experimental data available on the spectral properties of similar Bi-related centers in several hosts [18–22]. These centers are not related to IR luminescence and are of no interest for our investigation, since both the absorption and luminescence bands of the centers fall in the host self-absorption range.

According to the calculations, both  $\text{Bi}^0$  atoms and  $\text{Bi}^+$  ions are not stable in interstitial positions of  $\text{GeS}_2$  network. In the regular network interstitial Bi atoms tend to form bonds with the surrounding S atoms giving rise to network rearrangement with the above-mentioned  $\text{Bi}^{3+}$  and  $\text{Bi}^{2+}$  substitutional centers formed. The energy gain of such a rearrangement is estimated to be about 0.9 eV per unit cell. Therefore in  $\text{GeS}_{2-x}$  based glasses the IR luminescence is unlikely to be caused by interstitial  $\text{Bi}^+$  ions. Notice that the characteristic luminescence band of  $\text{Bi}^+$  ions is known from the experimental and theoretical data to be located near  $1 \mu\text{m}$  [15, 16, 23].

On the other hand, the calculations show that if an interstitial Bi atom occurs in  $\text{GeS}_2$  network in vicinity of such an intrinsic defect as a S vacancy,  $\equiv\text{Ge}-\text{Ge}\equiv$ , a complex of the interstitial  $\text{Bi}^0$  atom with the vacancy,  $\equiv\text{Ge}-\text{Bi}-\text{Ge}\equiv$ , is formed instead of the  $\text{Bi}^{3+}$  and  $\text{Bi}^{2+}$  substitutional centers. The total energy of the unit cell with such a complex is estimated to be about 0.6 eV lower than that of the unit cell with separated  $\text{Bi}^{3+}$  (or  $\text{Bi}^{2+}$ ) center and S vacancy. In this complex center bismuth turns out to be in the state close to monovalent state due to redistribution of electron density. Effective electronic charge  $\approx -0.8|e|$  is displaced from Bi and Ge atoms towards the area between Bi and Ge atoms, and to a lesser extent into the area between both Ge atoms. Thus a three-center system is formed consisting of a Bi atom and two Ge atoms with a coordination-type bonding between three atoms. In a rough approximation, basing on the described electron density redistribution, the complex may be considered as a pair of charged centers, the interstitial positively charged ion,  $\text{Bi}^+$ , adjacent to the negatively charged S vacancy,  $\equiv\text{Ge}^{\ominus}-\text{Ge}\equiv$ . This makes it possible to describe the electronic structure of the center in terms of a crystal field model similar to ones used previously for Bi-related centers in  $\text{TlCl}:\text{Bi}$ ,  $\text{CsI}:\text{Bi}$  [15],  $\text{SiO}_2:\text{Bi}$  and  $\text{GeO}_2:\text{Bi}$  [16], and in  $\text{AgCl}:\text{Bi}$  [17]. The ground state and the first two excited states of the  $\text{Bi}^+$  ion are known to arise from the triplet state,  $^3\text{P}$ , (electron configuration  $6s^2p^2$ ) split by strong intra-atomic spin-orbit interaction in three components, the ground state,  $^3\text{P}_0$ , and excited states,  $^3\text{P}_1$  and  $^3\text{P}_2$ , with the energies of about 13300 and 17000  $\text{cm}^{-1}$  in a free ion, respectively. These states can be further split and mutually mixed under the influence of the crystal field of the  $\text{Bi}^+$  ion environment in the

glass network. For the "Bi — vacancy" complex such an axial crystal field caused by a charged vacancy turns out to be strong. In an axial crystal field the ground state of  $\text{Bi}^+$  is not split, and the  $^3\text{P}_1$  and  $^3\text{P}_2$  excited states are split into two and three levels, respectively. The dipole transitions between the ground and excited states forbidden in the free ion become weakly allowed due to mixing of the wave functions. A relatively small (in comparison with Bi-related centers in other hosts) IR luminescence lifetime can be explained by a relatively high degree of  $\text{Bi}^+$  ion perturbation by the vacancy crystal field and, respectively, a significant state mixing. For example, our calculations [16] similar to the present ones have shown that in the complex center formed by interstitial Bi atom and anion vacancy in the  $\text{GeS}_2$  network the bonding is noticeably stronger than in similar centers in  $\text{SiO}_2$  or  $\text{GeO}_2$  networks.

The calculated levels and transitions in the complex center formed by the interstitial Bi atom and the S vacancy are shown in Fig. 4. The Stokes shift of the luminescence is found to be small, at least for the longest-wave transitions. This can be explained by relatively small admixture of Ge electronic states to the wave functions of this complex, so that small displacement of the Bi atom does not result in a noticeable change of electronic states of the complex. Thus, one expects the "Bi — vacancy" complex in the  $\text{GeS}_2$  network to cause IR luminescence bands near  $1.9 \dots 2.1 \mu\text{m}$  and  $1.5 \dots 1.8 \mu\text{m}$ , when excited both at the same absorption wavelength and in three absorption bands in the  $0.9 \dots 1.3 \mu\text{m}$  range.

#### IV. CONCLUSION

Basing on the above-mentioned total energy estimations it may be concluded that bismuth occurs in reg-

ular  $\text{GeS}_2$  network mainly as trivalent ( $\text{Bi}^{3+}$ ) substitutional centers, and, probably, as divalent ( $\text{Bi}^{2+}$ ) ones. However, centers formed by interstitial Bi atoms and S vacancies would be expected to occur in sulfur-deficient network, and only such complexes may give rise to the bismuth-related IR luminescence. Such a center may be considered as an interstitial  $\text{Bi}^+$  ion adjacent to negatively charged S vacancy. Comparison of the calculation results with the experimental data allow us to suggest that these complexes make the main contribution to the IR luminescence in  $\text{GeS}_{2-x}:\text{Bi}$  glasses.

Arsenic addition to Ge-S glass significantly enhances its resistance to crystallization and made it possible to draw optical fibers. Arsenic also significantly increased the intensity of luminescence. Such an increase in luminescence intensity in the arsenic-containing glasses can be explained by a decrease in concentration of Bi ions with oxidation degree higher than 1 due to reduction properties of arsenic. Furthermore, arsenic occurs in the glass network mainly in the form of threefold atoms and prevents the formation of the above-described substitution centers  $\text{Bi}^{3+}$  and  $\text{Bi}^{2+}$  centers. Sulfur deficiency in As-Ge-S compositions may promote the formation of S vacancies and complexes with interstitial Bi atoms.

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